

Polymerization of Dienes and Olefins Under the
Action of Cobalt Oxides and Diethyl Aluminum Halides, and a Study of the
Structure of Polymers

67919

SOV/20-129-5-29/64

aluminosilicate, the amount of the 1-2-members in the chain rises. Due to the high content of 1-4-members this polybutadiene has a low vitrification temperature (down to -115°). Isoprene is polymerized more slowly and at higher temperatures (at about 40°) as compared to butadiene. Here too, the process runs more slowly with the use of aluminosilicate as carrier. It may be observed from table 1 that both the microstructure of polyisoprene and the vitrification temperature are not changed appreciably by the concentration of the aluminum-organic compound nor by the ratio between cobalt oxide and aluminum diethyl halide. Fairly large amounts (17-18%) of isopropenyl side-groups increase the vitrification temperature of the polymer considerably. The total content of 1-4-members is about 80%; their major part is in the trans-position. A further strong retardation of polymerization takes place in the transition to higher dienes. α -butene is not quickly polymerized at room temperature and does form no more than a caoutchouc-like substance. Neither styrene nor α -methyl styrene are polymerized by the procedure de-

Card 3/4

Polymerization of Dienes and Olefins Under the
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Structure of Polymers

67919

SOV/20-129-5-29/64

scribed. Finally the authors state that no gaseous hydro-
carbon products are formed in the interaction between co-
balt oxides and an aluminum-organic compound at 0 to 80°. 4
There are 1 table and 9 references, 5 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk
SSSR (Institute of High-molecular Compounds of the Academy
of Sciences, USSR)

SUBMITTED: September 5, 1959

Card 4/4

15.9210

5.3831

5(3)

AUTHORS:

Tinyakova, Ye. I., Dolgoplosk, B. A., ⁶⁸¹⁶⁴ SOV/20-129-6-30/69
Corresponding Member, AS USSR,
Kovalevskaya, R. N., Zhuravleva, T. G.

TITLE:

Polymerization¹⁵ and Copolymerization of Dienes and Olefines on
a Chromium Oxide Catalyst

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 6, pp 1306 - 1308
(USSR)

ABSTRACT:

The authors (Tinyakova and Dolgoplosk) proved in a previous paper (Ref 1) that polymerization of butadiene and isoprene on a chromium oxide catalyst yields crystalline polymers containing only 1 - 4 links in trans position in the chain. Polymers of pentadiene-1 - 3, of α -butene, as well as a copolymer of dienes and olefines which are formed by polymerization on the above catalyst are described in the paper under review. Polymerization and copolymerization were carried out under conditions equal to those of the previous experiments (Ref 1). Contrary to butadiene and isoprene, pentadiene-1 - 3 yields an amorphous polymer, soluble in benzene, specific weight = 0.89. Its vitrification temperature is -60°C, its unsaturation 97% of the

Card 1/3

68164

Polymerization and Copolymerization of Dienes and
Olefines on a Chromium Oxide Catalyst

SOV/20-129-6-30/69

theoretical value. Fragments connected in position 3-4 are missing in its chain. Most of the 1 - 4 links are deposited in a trans position. On a chromium oxide catalyst, α -butene yields a crystalline fibrous polymer partially soluble in hot toluene and boiling diethyl ether (about 30%); its specific weight is 0.96. Figure 1 shows the dispersion curves of X-rays on poly- α -butene between 20 and 150°. A distinct maximum proves the crystalline structure of the polymer. A. N. Andreyeva carried out the radiosopic investigation by means of the X-ray apparatus of type URS-50. The crystals melt at about 140°. Modification I exists up to 40°, modification II between 60 and 140°. Both modifications exist at about 50°. In the case of natural rubber and gutta-percha, the vitrification temperature of polymers with cis and trans configurations of the links is practically equal (-71°). Vitrification at -110° was to be expected in the case of transpolybutadiene. Table 1 shows that the polymer loses its crystallizing power due to copolymerization of butadiene or isoprene with other compounds. The polymer becomes highly elastic. These transformations are due to the destruction of the trans-1-4 structure. Amorphous elastic products are formed by copolymeriza-

Card 2/3

Polymerization and Copolymerization of Dienes and
Olefines on a Chromium Oxide Catalyst

68164
SOV/20-129-6-30/69

tion of mixtures of butadiene with isoprene and pentadiene-1 - 3 as well as of isoprene with ethylene. Their vitrification temperature ranges between the vitrification temperatures of the polymers from corresponding monomers (Table 1). In all cases, a monomer mixture polymerizes more slowly than each individual monomer by itself (Fig 2). All butadiene and isoprene links in the chain are only in trans-1 - 4 position as was proved by infrared spectroscopy (photographs by K. V. Nel'son) in the elastic amorphous polymer from butadiene and isoprene (equimolar). The polymer contains 55% of butadiene links as was computed from the unsaturation values (Table 1). The vitrification temperature of the amorphous isoprene ethylene transpolymer is lower than that of natural rubber. In the case of butadiene, a highly elastic state could be attained only by copolymerization with isoprene and pentadiene-1 - 3. There are 2 figures, 1 table, and 5 references, 3 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences, USSR)

SUBMITTED: September 5, 1959
Card 3/3

KROPACHEV, V.A.; DOLGOPILOSK, B.A.; GELLER, N.M.; ROZINOV, Ya.M.

Use of organoaluminum compounds as catalysts for the polymerization of 3,3'-bis(chloromethyl)oxacyclobutane and isobutylene.
Vysokom.soced. 1 no.12:1844-1847 D '59. (MIRA 13:5)

1. Institut vysokomolekulyarnykh soedineniy AN SSSR.
(Aluminum organic compounds) (Oxetane)

"APPROVED FOR RELEASE: 06/13/2000

CIA-RDP86-00513R000410810016-0

APPROVED FOR RELEASE: 06/13/2000

CIA-RDP86-00513R000410810016-0"

.. DOL GOPLOSK, B. A.

SOV/4982

International symposium on macromolecular chemistry, Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii SSSR, Moskva, 14-18 iyunya 1960 g.; doklady i avtoroferaty. Sektsiya I. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18, 1960; Papers and Summaries. Section I.) [Moscow, Izd-vo AN SSSR, 1960] 346 p. 5,500 copies printed.

Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry

Tech. Ed.: T. V. Polyakova.

PURPOSE: This collection of articles is intended for chemists and researchers interested in macromolecular chemistry.

COVERAGE: This is Section I of a multivolume work containing scientific papers on macromolecular chemistry in Moscow. The material includes data on the synthesis and properties of polymers, and on the processes of polymerization,
Card 1/9

International Symposium (Cont.)

SOV/4982

copolymerization, polycondensation, and polyrecombination. Each text is presented in full or summarized in French, English, and Russian. There are 47 papers, 28 of which were presented by Soviet, Rumanian, Hungarian, and Czechoslovakian scientists. No personalities are mentioned. References accompany individual articles.

TABLE OF CONTENTS:

| | |
|---|----|
| Pino, P., G. P. Lorenzi, and L. Lardicci (Italy). Isotactic Polymers of Optically Active α -Olefins | 5 |
| Goldenberg, N., and R. Istratou (Rumania). Influence of Synthesis Conditions on Some Physicochemical Properties of Polypropylene | 9 |
| Tinyakova, Ye. I., B. A. Dolgoplosk, T. G. Zhuravleva, R. N. Kovalevskaya, and T. N. Kuren'gina (USSR). The Synthesis of Cis- and Trans-Diene Polymers on Oxide Catalysts and a Study of Their Structure and Properties | 13 |
| Butler, K., P. R. Thomas, and G. J. Tyler (Great Britain). Stereospecific Polymerization of Some Polar Vinyl Monomers | 21 |
| Card 2/9 | |

International Symposium on Macromolecular Chemistry (Cont.) SOV/4983

Dolgoplosk, B.A. (USSR). Study of the Factors Leading to the Degradation of Chain Structure During the Ionic Polymerization of Dienes 346

Yerusalimskiy, B.L., Wang Fo-sung, and A.P. Kavunenko (USSR). Study of the Interaction of Organomagnesium Compounds With Salts of Heavy Metals and the Use of Organomagnesium Compounds and Their Complexes to Stimulate Polymerization 355

Finch, G.A. (Great Britain). Catalysts for Vinyl Polymerization From Rare Metal Halide Complexes 364

Santo, I., and K. Gal (Hungary). The Effect of Organic Inner Complexes of Some Metals of Variable Valence on the Kinetics of the Polymerization of Vinyl Compounds 366

Bresler, S.Ye., M.I. Mosevitskiy, I. Ya. Poddubnyy, and Shih Kuang-i (USSR). Study of Some Details of the Mechanism of Polymerization Under the Action of Complex Catalysts 372

Card 8/12

DOL G OPL OSK, B. A.

PART I BOOK EXPLANATION 807/995

International symposium on macromolecular chemistry. Moscow, 1960.
 Macromolecular symposium on macromolecular chemistry. USSR, Moscow, 14-18 June 1960 at Academy of Sciences, Section II. (Int. national symposium on macromolecular chemistry held in Moscow, June 14-18, 1960; papers and summaries) Section II. [Moscow, Izd-vo AN SSSR, 1960] 559 p. 5,500 copies printed.
 Sponsoring Agency: The International Union of Pure and Applied Chemistry, Commission on Macromolecular Chemistry
 Tech. Ed.: I.A. Prashova.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high-molecular compounds.

CONTENTS: This is Section II of a multivolume work containing papers on macromolecular chemistry. The papers in this volume treat mainly the kinetics of various polymerization reactions initiated by different catalysts or induced by radiation. Among the research techniques discussed are electron paramagnetic resonance, spectroscopy and light-scattering interpretation. There are summaries in English, French and Russian. No personalities are mentioned. References follow each article.

| | |
|---|-----|
| Mikhail, B., and J. Kerpoczki (Russia). On the Mechanism of the Formation Reaction of Stereoregular Polymers | 302 |
| Glenn, A., and O. Chyres (Hungary). On the Kinetics of a Reaction on Ziegler Catalysts | 310 |
| Vinograd, O., M. Mark, and I. Trakova (Czechoslovakia). Kinetics of the Polymerization of Isobutylene on a Heterogeneous Catalyst | 322 |
| Soest, Y. (Czechoslovakia). Heterogeneous Catalysts for the Polymerization of Alpha Olefins | 330 |
| Vinograd, O., J. Jancus, E. Vile, and O. Simcik (Czechoslovakia). The Effect of Dimer Type Impurities on the Polymerization of Propylene. Catalyzed by the System Titanium Trichloride-Triethylaluminum | 337 |
| Polyglock, R. (USSR). Study of the Factors Leading to the Degradation of Chain Structure During the Ionic Polymerization of Dienes | 346 |
| Tereshinskiy, B., Veng Pong-ang, and A.P. Karyuchko (USSR). Study of the Interaction of Organometallic Compounds With Salts of Heavy Metals and the Use of Organometallic Compounds and Their Complexes to Stimulate Polymerization | 355 |
| Barto, I., and E. Gai (Hungary). The Effect of Organic Imer Complexes of Iron Metals of Variable Valence on the Kinetics of the Polymerization of Vinyl Compounds | 366 |
| Bresler, S. Ye., N.I. Koveritskiy, L. Ya. Podlubnyy, and Shih Kung-i (USSR). Study of Some Details of the Mechanism of Polymerization Under the Action of Complex Catalysts | 372 |
| Tsvetkov, V. J., S. Ya. Mavrik, S. S. Bontova, and M. G. Chumachenko (USSR). Stereospecificity and the Optical Properties of Polymers | 378 |
| Kirshvyn, T. M., Ye. Ye. Gotsilya, and O. B. Pritum (USSR). The Microviscosity of Polymers and Methods of Study | 388 |
| Altin, A. A., A. Z. Shcheglov, N. S. Yakovlev, and J. P. Michelson (USSR). On Carbonium and Carbanion Polymerization Mechanisms Under the Effects of Gamma Radiation | 398 |
| Shubin, V. A., and V. A. Eshkov (USSR). Polymerization Processes in Insoluble Molecular Dispersions | 403 |
| Matukaitis, Z., V. Kojila, and I. P. (Czechoslovakia). Kinetics of the Polymerization of Formaldehyde | 403 |
| Vasely, E. (Czechoslovakia). On the Mechanism of Ionic Polymerization | 403 |
| Klimal, Z., and A. Janda (Czechoslovakia). On the Role of Homopolymer Compounds in the Cationic Polymerization of Isobutylene | 403 |

31

45

DOLGOPILOSK, B. A., ZHURAVLEVA, T. G., KOVALEVSKAYA, R. N., KURENGINA, T. N. and

TINYAKOVA, E. I. (USSR)

Sintez tsis- i trans-polimerov dienov nad okisnymi katalizatorami
i izucheniye ikh struktury i svoystv

The synthesis of cis- and trans-diene polymers on oxide catalysts
and a study of their structure and properties

IUPAC S I:13-20

report presented at the Intl. Symposium on Macromolecular Chemistry, Moscow,
14-18 June 60.

ALFEROVA, L.V.; DOLGOPILOSK, B.A.; KROPACHEV, V.A.

Mechanism of the decomposition of aliphatic .. aromatic tria-
zenes under the influence of acids and water. Vysokom.soad.
2 no.1:3-12 Ja '60. (MIRA 13:5)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Triazene)

ALFEROVA, L.V.; DOLGOPILOSE, B.A.; KHOPACHEV, V.A.

Decomposition of diazoaminobenzene in hydrocarbon media under the influence of organic acids, and use of the reaction in initiating polymerisation. Vysokom.soed. 2 no.1:67-74 Ja '60. (MIRA 13:5)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR.
(Benzene) (Acids, Organic) (Polymerization)

Dolgoplosk, B. A.

5.3200

82044
S/062/60/C00/02/03/012
B003/B066

AUTHORS: Dolgoplosk, B. A., Yeruslimskiy, B. L., Kuren'gina, T. N.,
Tinyakova, Ye. I.

TITLE: Reactions of Free Radicals in Solutions. 15th Report.
Destruction Mechanism of Polymers by Free Radicals

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk.
1960, No. 2, pp. 311 - 316

TEXT: The authors investigated the destruction of polyisobutylene dissolved in ethyl benzene under the action of disulfides, benzoyl peroxide, isopropyl benzene-hydroperoxide, triazenes, dimethyl-diphenyl-tetrazene, iron- and cobalt naphthenate. The destructive effect of the individual agents may be seen from the diagrams in Figs. 1, 2, and 3. The following conclusions may be drawn from the investigations and pertinent papers by other authors: The destructive effect is most intense in such free radicals as are especially active in the reaction of H-separation. The destruction takes place in such a manner that first a H-atom is separated from the polymer chain and, secondly, the C-C bonds of the polymer radical

Card 1/2

Reactions of Free Radicals in Solutions. S/062/60/000/02/08/012
15th Report. Destruction Mechanism of Polymers by Free Radicals B003/B066

thus formed are spontaneously freed. The authors mention a paper by
L. M. Romanov (Ref. 2). There are 3 figures and 14 references: 8 Soviet,
4 American and British, and 2 German.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk
SSSR (Institute of High-molecular Compounds of the Academy
of Sciences USSR)

SUBMITTED: June 19, 1958

Card 2/2

S/062/60/000/03/04/007
B008/B006

AUTHORS: Van Fo-sun, Dolgoplosk, B. A., Yerusalskiy, B. L.
TITLE: Reactions of Organo-metallic Compounds With Salts of Heavy Metals. 1. Interaction of Ethyl Magnesium Bromide With Halides of Titanium and Cobalt

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 3, pp. 469-473

TEXT: An investigation of the interaction of ethyl magnesium bromide with titanium trichloride and titanium tetrachloride in the presence of acceptors for free radicals was carried out. As such, nitrogen oxide, styrene, and α -methyl styrene were used. The experiments were carried out in the apparatus schematically shown in Fig. 1. Data on the interaction of magnesium ethyl bromide and titanium tetrachloride at 20°C in the presence of the above acceptors are given in Table 1. Data on the interaction of ethyl magnesium bromide and titanium trichloride at 100°C in the presence of nitrogen oxide and α -methyl styrene are listed in Table 2. Also, the interaction of ethyl magnesium bromide and cobalt

Card 1/2

Reactions of Organo-Metallic Compounds With
Salts of Heavy Metals. 1. Interaction of
Ethyl Magnesium Bromide With Halides of
Titanium and Cobalt

S/062/60/000/03/04/007
B008/B006

chloride in the presence of the three above-mentioned acceptors in the temperature range -20°C - 40°C was investigated (Table 3). The data given in Tables 1 to 3 allow the assumption that the reaction of ethyl magnesium bromide with titanium- and cobalt salts - at least at the temperatures applied in the experiments - does not proceed via radical stages. It was seen in the experiments that the total yields of ethane and ethylene, and their proportion are not affected by the presence of the above acceptors. The authors mention a paper by N. V. Kondyrev and D. A. Fomina (Ref. 1), and one by Yu. V. Koryakin (Ref. 11). There are 1 figure, 3 tables, and 12 references, 4 of which are Soviet.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk
SSSR (Institute of High-molecular Compounds of the
Academy of Sciences, USSR)

SUBMITTED: July 14, 1958

Card 2/2

15,9201 2109,2209,1372

84511

S/190/60/002/004/012/020
B004/B056

AUTHORS: Van Fo-sun, Dolgoplosk, B. A., Yeruslimskiy, B. L.
TITLE: Polymerization of Isoprene Under the Influence of
Organomagnesium Compounds
PERIODICAL: Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 4,
pp. 541-545

TEXT: The authors report on the polymerization of isoprene in cumene carried out by means of ether-free butylmagnesium chloride, bromide, iodide, dibutylmagnesium, and mixtures of butylmagnesium iodide and dibutylmagnesium, as well as of phenylmagnesium chloride and diphenylmagnesium at 90°C and a concentration of the monomeric isoprene of 60 mole%. Results are given in Table 1: yield, 4 - 50%; duration of the reaction, 20 - 40 hours; ratio between monomer and organomagnesium compound, 1 : 0.007 - 1 : 0.044; vitrification temperature, -3 to -10°C; intrinsic viscosity, 0.75 - 0.95; degree of unsaturation, 77 - 83%; content of 3,4-bonds, 93 - 98% (determined by means of infrared

Card 1/3

84511

Polymerization of Isoprene Under the
Influence of Organomagnesium Compounds

S/190/60/002/004/012/020
B004/B056

spectroscopy by Ye. I. Pokrovskiy at the authors' institute). The polyisoprene obtained in this way was perfectly soluble in benzene, probably because of intramolecular cyclization of the polymer chain. It mainly contained 3,4-bonds, so that the vitrification temperature is considerably increased in comparison to 1,4-polyisoprene. The kind of the halogen and radical of the organomagnesium compound did not affect the structure of the polymer. Fig. 1 shows the infrared spectrum of a polyisoprene sample. By adding complexing reagents, such as diethyl ether or triethylamine, the polymerization is retarded with an increase in the concentration of the reagents (Fig. 2, Table 2). Besides, a decrease in 3,4-bonds to 83 - 88% occurs (Table 3). In the experimental part, the authors describe the synthesis of ether-free organomagnesium compounds in cumene at 130 - 140°C, as well as in paraffin hydrocarbons in sealed ampoules at 135°C. There are 2 figures, 3 tables, and 5 references: 1 Soviet, 1 US, 1 British, and 2 German. J

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(Institute of High-molecular Compounds AS USSR)

Card 2/3

Polymerization of Isoprene Under the
Influence of Organomagnesium Compounds

SUBMITTED: December 18, 1959

84511

S/190/60/002/004/012/020
B004/B056

X

Card 3/3

Dolgoplosk, B. A.

81934

S/062/60/000/06/05/011
B020/B061

5.3700C

AUTHORS:

Kropachev, V. A. Dolgoplosk, B. A., Geller, N. M.,
Zelenina, M. N.

TITLE:

Reactions Between Organo-metallic Compounds and Heavy Metal
Salts. II. Interaction of Lithium-ethyl With Cobalt and
Titanium Halides

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniya khimicheskikh nauk,
1960, No. 6, pp. 1044 - 1048

TEXT: The reaction of ethyl-lithium with titanium tetrachloride and cobalt chloride is examined here at 20° in hydrocarbon solvents and in the presence of unsaturated hydrocarbons as free-radical acceptors. In the case of radical stages, the said reaction cannot lead to the formation of ethane and ethylene. Similarly, the reaction of organo-magnesium compounds with metal halides was examined earlier (Ref. 12). All reactions were carried out in solutions (in benzene, metaxylol) at 20°. In connection with the fact that α-methylstyrene polymerizes under reaction conditions on the

Card 1/3

Reactions Between Organo-metallic Compounds and Heavy Metal Salts. II. Interaction of Lithium-ethyl With Cobalt and Titanium Halides

81934

S/062/60/000/06/05/011

B020/B061

action of the ethyl-lithium and TiCl_4 , the α -methylstyrene was gradually introduced to the reaction mixture, thus maintaining a sufficient quantity of free olefin in the mixture at all times. The products of the reaction of ethyl-lithium with cobalt chloride (Table 1) and with TiCl_4 (Table 2) at 20° are given. On the reaction of ethyl-lithium with cobalt chloride, equimolar quantities of ethane and ethylene are liberated, whilst only ethane is liberated when reacting with TiCl_4 , the ethylene being polymerized.

The introduction of acceptors in no case affected the composition of the reaction products. The performance of the experiments is exactly described in the experimental part (Fig. 1, reaction vessel with mixer), and hints are given for carrying out the reaction of ethyl-lithium with TiCl_4 and cobalt chloride. The results obtained show that the formation of ethane and ethylene is not connected with radical interstages. There are 1 figure, 2 tables, and 13 references: 4 Soviet, 7 USA, and 2 German.

Card 2/3

Reactions Between Organo-metallic Compounds and Heavy Metal Salts. II. Interaction of Lithium-ethyl With Cobalt and Titanium Halides

81934

S/062/60/000/06/05/011
B020/B061

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk
SSSR (Institute of High-molecular Compounds of the Academy
of Sciences USSR)

SUBMITTED: December 1, 1958

✓

Card 3/3

S/062/60/000/009/014/021
B023/B064

AUTHORS: Yerusalimskiy, B. L., Vavunenko, A. P., and Dolgoroskiy, B.A.
TITLE: Reactions of the Free Radicals in Solutions. Communication
17. Effect of the Viscosity of the Medium on the Primary
Recombination of Free Radicals
PERIODICAL: Izvestiya Akademii nauk SSSR Otdeleniye khimicheskikh
nauk, 1960, No. 9, pp. 1672-1674

TEXT: The authors investigated in how far the methane- and methyl aniline yields depend on the molecular weight and concentration of the polymer in the case of thermal splitting of methyl-phenyl triazene in the cumene - polystyrene system. As is shown by a previous paper of the authors (Ref.2), in solutions with 60% polystyrene (molecular weight 5000 to 200,000), the reaction leads to a reduction of the methane yield as compared to the data obtained from the use of a pure solvent. The methyl aniline yield remains, however, the same as that obtained in the absence of the polymer. Only in the solution of polystyrene with a molecular weight of 600,000, and a polymer concentration of 60%, the methyl aniline yield increases, while the

Card 1/3

Reactions of the Free Radicals in Solutions.
Communication 17. Effect of the Viscosity of
the Medium on the Primary Recombination of
Free Radicals

S/062/60/000/009/014/021
B023/B064

methane yield decreases considerably (Table 1). Consequently, the change of yields in methane solutions, containing polystyrene with a molecular weight of up to 200,000, cannot be considered as a result of the increase in viscosity of the medium. This would have certainly led to a higher yield of the product of methyl aniline primary recombination. The reduction of the yield is more likely to be due to the difference between the relative activity of polystyrene and that of cumene than to hydrogen donors. This is in agreement with published data, according to which the H atoms in polystyrene are less mobile than in cumene (Ref. 3). The authors proved that also in systems containing considerably lower polystyrene concentrations, the methane yield is reduced. The amount of the yield depends, as is shown in Table 2, on the concentration only. The molecular weight of the polymer has no effect upon the amount of the yield. In systems with a high viscosity, the importance of the primary recombination of free radicals increases. This becomes obvious by the fact that the methyl aniline yield increases, while the methane yield decreases at the same time. There are 2 tables and 5 references:

Card 2/3

Reactions of the Free Radicals in Solutions.
Communication 17. Effect of the Viscosity of
the Medium on the Primary Recombination of
Free Radicals

S/062/60/000/009/014/021
B003/B064

4 Soviet and 1 US.

ASSOCIATION: Institut vysokomolekulyarnykh soedineniy Akademii nauk SSSR
(Institute of Highmolecular Compounds of the Academy of
Sciences USSR)

SUBMITTED: April 7, 1959

Card 3/3

87168

S/062/60/000/012/007/020
B013/B055

5 3760

AUTHORS: Zgonnik, V. N., Krcpachev, V. A., Nikolayev, N. I.,
and Dolgoplosk, B. A.

TITLE: Reactions of Organometallic Compounds With Heavy-metal
Salts. IV. Interaction of Ethyl Lithium With Titanium
Trichloride

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 12, pp. 2157-2161

TEXT: The present work is a study of the reaction of ethyl lithium with the purple, crystalline α -modification of titanium trichloride in hydrocarbon mediums. The reaction was performed at 0, 20, 55, and 100°C applying various molar ratios of ethyl lithium and titanium trichloride. The yields and compositions of the gaseous reaction products are summarized in Table 1. It can be seen that the ratio of the reactants has a stronger influence on the composition of the gases than the reaction temperature. The yields of gaseous reaction products increase with increasing temperature and at 100°C approach the theoretical amount with regard to the initial ethyl lithium.

Card 1/3

87168

Reactions of Organometallic Compounds With
Heavy-metal Salts. IV. Interaction of Ethyl
Lithium With Titanium Trichloride

S/062/60/C00/012/007/020
B013/E055

✓

Even at low temperatures, gas formation occurs within a few minutes. Gas yields are about 10-20% at low temperatures (Table 1) and the gas contains mainly ethane. This might give rise to the conclusion that simultaneously formed ethylene is partly polymerized. It was shown, however, that ethylene polymerization does not occur. At temperatures around 100°C and above the possibility of thermal decomposition (Ref. 9) must be taken into consideration. The reaction of ethyl lithium with titanium trichloride is practically instantaneous at 100°C, whereas the thermal decomposition under the same conditions reaches an extent of 25% only after 14 h. The composition of the gases obtained in these two cases is shown in Table 2 for which two characteristic experiments were selected. Hydrolysis of the reaction products of ethyl lithium and titanium trichloride yielded large quantities of hydrogen which in some cases by far exceeded the stoichiometric amount. The precipitate dissolves during hydrolysis. This indicates that the reaction products contain no metallic titanium. Lithium hydride, formed during the decomposition of ethyl lithium according to the scheme $\text{LiC}_2\text{H}_5 \rightarrow \text{LiH} + \text{CH}_2=\text{CH}_2$, may constitute another source of hydrogen. This decomposition actually occurs above 100°C. As has been mentioned, the decomposition of ethyl lithium

Card 2/3

87168

Reactions of Organometallic Compounds With ~~9062/60/000/012/007/020~~
Heavy-metal Salts. IV. Interaction of Ethyl ~~B013/B055~~
Lithium With Titanium Trichloride

proceeds much more rapidly and at lower temperatures in the presence of titanium trichloride. At 55-100°C this reaction is very rapid. In experiments at these temperatures, 1 mole titanium trichloride caused decomposition of up to 7 mole ethyl lithium (Table 3). The results obtained show that titanium halides catalyze the decomposition of ethyl lithium to ethylene and lithium hydride. There are 1 figure, 3 tables, and 11 references: 2 Soviet, 3 German, and 7 US. ✓

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR
(Institute of High-molecular Compounds of the Academy of Sciences USSR)

SUBMITTED: July 11, 1959

Card 3/3

67892

5.3831
5(3), 15(9)
AUTHORS:

Kropacheva, Ye.N., Dolgoplosk, B.A., S/020/60/130/06/020/059
Corresponding Member AS USSR, B011/B015
Kuznetsova, Ye.M.

TITLE:

Investigation of the Rate of Addition of Lithium Ethyl to
Styrene and Isoprene in the Course of the Polymerization
Process

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 6, pp 1253-1255
(USSR)

ABSTRACT:

The aim of this paper is to prove that the original organo-metallic compound is not added at once to the diene monomer as shown by data of S.Ye.Bresler and collaborators (Ref 1). The authors carried out their experiments in pure anhydrous argon at 250-300°. For this purpose they used a special reaction apparatus (Fig 1). Samples were taken from the reaction vessel within certain intervals, and by means of them the amount of the polymer formed was determined as well as that of the lithium ethyl which did not enter the reaction. The molar ratio between lithium ethyl and monomer was 1/150 (with isoprene) and 1/100 (with styrene). Figure 2 shows the polymerization kinetics of

Card 1/3

67892

Investigation of the Rate of Addition of Lithium S/020/60/130/06/020/059
Ethyl to Styrene and Isoprene in the Course of B011/B015
the Polymerization Process

styrene at $+1^{\circ}$, figure 3 the same at 24° for isoprene. These data indicate that the addition of lithium ethyl to the monomer proceeds gradually in the course of the entire process of polymerization. The polymerization of styrene and isoprene in the presence of tetrahydrofuran with which organolithium compounds form complexes was investigated in a similar way. For this purpose, solutions in heptane were used which contained 16% of styrene (at -20°) or 20% of isoprene (at $+25^{\circ}$). The curves III in figures 2 and 3 show the consumption of lithium ethyl in the course of the polymerization of styrene and isoprene, respectively, in the presence of tetrahydrofuran (1 : 5). Curves IV show the polymer yield. They indicate the rapid acceleration of the primary act of addition of lithium ethyl to the monomer brought about by tetrahydrofuran. Thus, polymerization is also accelerated. The "living" polymer chain thus developing remains capable of further growing during a long time, even if the entire lithium ethyl and the monomer are consumed. Curves V and VI (Fig 3) indicate that the polymerization process sets in with normal rapidity when isoprene (20%) was filled up in heptane. The data set up by the authors deal

Card 2/3

67892

Investigation of the Rate of Addition of Lithium Ethyl to Styrene and Isoprene in the Course of the Polymerization Process S/020/60/130/06/020/059 B011/B015

with the concentration range of lithium ethyl between 0.7 and 1% by mole (referred to the monomer). A considerable dependence of the rates of the primary addition act and the growth of chain on the association degree of lithium ethyl is possible. This degree decreases with falling concentration of the organometallic compound in solution (Ref 10). There are 3 figures and 10 references, 8 of which are Soviet.

ASSOCIATION: Nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V. Lebedeva (Scientific Research Institute of Synthetic Rubber imeni S.V. Lebedev)

SUBMITTED: November 23, 1959

Card 3/3

5.3300

69507

AUTHORS:

Boldyreva, I. I., Dolgoplosk, B. A.,
Corresponding Member, AS USSR,
Kropacheva, Ye. N., Nel'son, K. V.

S/020/60/131/04/031/073
B011/B017

TITLE:

Cis-trans-isomerization of Natural Rubber Under the Influence of
Hydrogen Chloride and Ethyl Aluminum Dichloride

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 830-832 (USSR)

TEXT: The authors investigated the effect of anhydrous HCl and of ethyl aluminum chloride on a benzene solution of natural rubber under conditions which had been described earlier (Ref 1). HCl was introduced as a saturated benzene solution. The microstructure of each sample was characterized by means of the IR-absorption spectra. The quantitative content of cis- and trans-configurations was determined on the basis of the band 840 cm^{-1} . Since, due to the HCl addition, the non-saturation of the polymer is partly reduced, the relative content of the links of each configuration was calculated in % of the double bonds remaining in the polymer. Table 1, and figures 1 and 2 show the results. The authors emphasize that the data of the relative content of cis-trans-links only characterize the qualitative picture of the process since the accuracy of spectroscopic determinations sensibly decreases with decreasing non-saturation of the polymer. Since the solubility of the polymer is limited, it was not always possible to compensate for the decrease in the

Card 1/3

69507

Cis-trans-isomerization of Natural Rubber Under
the Influence of Hydrogen Chloride and Ethyl Alu-
minum Dichloride

S/020/60/131/04/031/073
B011/B017

number of double bonds by increasing the concentration of the polymer in solu-
tions. Table 1 shows that ethyl aluminum chloride as well as HCl exercise an
isomerizing effect on the polymer chain of natural rubber. The number of trans-
links increases with the concentration of the isomerizing agent. In both cases,
the isomerization is accompanied by a reduction of the non-saturation of the
polymer chain. In the case of aluminum chloride, this seems to be mainly due to
the intramolecular ring formation. HCl, however, reduces the non-saturation
only insofar as it is added to the double bond (Fig 1). The amount of HCl added
corresponds to the reduction of non-saturation of the chain. The non-saturation
continuously decreases with extension of the reaction time (Curve 1). In this
connection, the relative content of trans-links (Curves 2 and 3), and the
chlorine content in the polymer, increase steadily (Curve 3). Figure 2 shows
that the isomerization and the addition of HCl already start at -70° , and
that they considerably are accelerated in the case of a temperature rise. At
 60° , the total content of double bonds, and of added chlorine, is only 82%
of the theoretical content. This is apparently due to the ring formation. The
experiments of the authors show that under the described conditions cis-poly-
butadiene is not sensibly isomerized. The high sensitivity of cis-polyisoprene 7
to isomerization under the influence of ion catalysts is probably connected with

Card 2/3

69507

Cis-trans-isomerization of Natural Rubber Under
the Influence of Hydrogen Chloride and Ethyl Alu-
minum Dichloride

S/020/60/131/04/031/073
B011/B017

the iso-structure of the chain. The easier stereospecific synthesis of cis-poly-
isoprene as compared to that of cis-polybutadiene is probably also due to this
fact. There are 2 figures, 1 table, and 9 references, 2 of which are Soviet. X

ASSOCIATION: Nauchno-issledovatel'skiy institut sinteticheskogo kauchuka
im. S. V. Lebedeva
(Scientific Research Institute of Synthetic Rubber imeni S. V.
Lebedev)

SUBMITTED: October 26, 1959

Card 3/3

89024

S/020/60/135/004/021/037
B016/B062

11.2211

AUTHORS:

Dolgoplosk, B. A., Corresponding Member AN USSR,
Kropacheva, Ye. N., Khrennikova, Ye. K., Kuznetsova, Ye. I.,
and Golodova, K. G.

TITLE:

Polymerization of Dienes Under the Influence of Homogeneous
Catalytic Systems Containing Salts of Cobalt and Nickel

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 4, pp. 847-848

TEXT: The authors report on the considerable efficacy of homogeneous catalysts in the production of cis-polybutadiene from butadiene in benzene solution. The catalysts were hydrocarbon-soluble systems of cobalt chloride (concentration 0.005 - 0.01 percentage by weight, as referred to the monomer) in complex with pyridine or ethanol in combination with alkyl-, dialkyl-, and trialkyl aluminum chlorides. Polymerization takes place already at 0°C and 0.005 % cobalt chloride, the polymer structure being independent of temperature. The polymer yield rises with increasing concentration of the cobalt chloride, while the molecular weight of the polymer decreases. The polymerization rate is highest at a concentration of 0.01 %, X

Card 1/3

Polymerization of Dienes Under the Influence
of Homogeneous Catalytic Systems Containing
Salts of Cobalt and Nickel

89024

S/020/60/135/004/021/037
BC 16/B062

whereas the molecular weight in the entire concentration range studied decreases simultaneously with the acceleration of polymerization. The temperature rise from 5° to 30°C also reduces the molecular weight to 1/2 - 1/3. The role of the displacement reactions becomes much more considerable in the presence of lower olefins. For instance, approximately 1 % of β -butene (referred to the monomer) considerably decelerates the polymerization and reduces the molecular weight of the polymer from 150 000 to 90 000. On the strength of data on the microstructure of polybutadiene the authors found, depending on the catalyst system (Table 1, polymerization of divinyl), that the highest percentage of 1,4-members was obtained with diisobutyl aluminum chloride systems (97 %) and diethyl aluminum chloride systems. Triisobutyl aluminum considerably increases the number of 1,2-members (up to 70 %). Cobalt salts of stearic acid lead to an only inconsiderably deviating chain structure in the range of concentrations ensuring a homogeneous system. Polybutadiene produced in the presence of nickel stearate has a chain structure similar to that of cobalt stearate, but a lower molecular weight. If iron benzoate and stearate is used, the polymerization is considerably slower than with cobalt- and

X

Card 2/3

89024

Polymerization of Dienes Under the Influence
of Homogeneous Catalytic Systems Containing
Salts of Cobalt and Nickel

S/020/60/135/004/021/037
B016/B062

nickel salts. The cobalt systems are also effective in the polymerization of other diene-hydrocarbons, especially of isoprene. There are 2 figures, 1 table, and 7 references: 5 Soviet, 1 US, and 1 German.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: August 22, 1960

Card 3/3

28038

S/081/61/000/015/127/139
B102/B101

15.9201

AUTHORS: Reykh, V. N., Dolgoplosk, B. A., Tinyakova, Ye. I., Kalas, A. Ye.

TITLE: Properties of carboxyl-containing rubbers

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 15, 1961, 600, abstract 1577354 (Sb. "Vulkanizatsiya rezin izdeliy" Yaroslavl', 1960, 43 - 55)

TEXT: Results of preliminary tests of butadiene styrene CK-1-30(SK-1-30) divinyl and isoprene rubbers with additions of methacrylic acid are given. Rubbers from SK-1-30 surpassed the rubbers from CK-30 (SKS-30A) with respect to stability to pure-gum mixtures, thermal stability, resistance to thermal aging, widening of cuts, wear, and with respect to elasticity. Carboxyl-containing isoprene rubber shows the least heat release on repeated deformation. [Abstractor's note: Complete translation.] X

Card 1/1

DOLGOPLOSK, B.A.; KROPACHEVA, Ye. N.; KHRENNIKOVA, Ye.K.; KUZNETSOVA, Ye.I.;
GOLOGOVA, K.G.

Polymerization of dienes under the influence of homogeneous
catalytic systems containing cobalt and nickel salts. Dokl.
AN SSSR 135 no.4:847-848 '60. (MIRA 13:11)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo
kauchuka im. S. V. Lebedeva. 2. Chlen-korrespondent AN SSSR (for
Dolgoplosk).

(Clefins) (Polymerization)

DOLGOPLOSK, B. A., YERUSALIMSKIY, B. L., KROPUCHEVA, Ye.N.,
TINYAKOVA, Ye. L.

"Structure of Diene Polymers as a Function of the Nature
of Catalytic Systems"

Report presented at the Conference on International Symposium
on Macromolecular Chemistry. Montreal, Canada, 27 July to 1 August 61.

1. Institute for higher Molecular Compounds, Akademia
Nauk, SSSR, Leningrad, USSR.

DOLGOPLOSK, B.A.; TINYAKOVA, Ye.I.

Present-day problems of synthetic rubber; synthesis of rubber for
general purposes. Khim.prom. no.10:55-67 0 '61; (MIRA 15:2)
(Rubber, Synthetic)

15.8663

28279
S/062/61/000/010/016/018
B106/B101

AUTHORS: Bogomol'nyy, V. Ya., and Dolgoplosk, B. A.

TITLE: Use of the reaction of organodilithium compounds with metal halides for the synthesis of polymers with a conjugate system of double bonds

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 10, 1961, 1912

TEXT: It is known that the reaction of phenyl-magnesium halides with salts of metals of variable valency yields almost quantitative amounts of diphenyl (Ref. 1: see below): $C_6H_5MgI + Me^{n+1} \rightarrow C_6H_5 - C_6H_5 + Me^n$. It was shown that reactions of this type do not follow the radical mechanism (Ref. 2: Wang Fo-sung, B. A. Dolgoplosk, B. L. Yeruslimskiy, Izv. AN SSSR. Otd. khim. n., 1960, 469). In this connection, the above reaction proved suitable for the preparation of polymers from the corresponding bifunctional organometallic compounds. Publications show that oligophenylenes can be synthesized by reaction of orthodilithium benzene with heavy-metal halides

Card 1/3

20279

S/062/61/000/010/016/018
B106/B101

Use of the reaction of organodilithium...

(Ref. 3: G. Wittig, F. Bickelhaupt, Chem. Ber. 91, 683 (1958)). The present authors obtained polymers with a condensed system of double bonds by reaction of p-dilithium benzene, p-dilithium diphenyl, and dilithium tetraphenyl butadiene-1,3 with titanium, vanadium, and cobalt halides. The first two monomers were synthesized by reaction of equimolecular amounts of a suspension of the corresponding dilithium derivatives in diethyl ether, hexane, or benzene with titanium tetrachloride or vanadium oxychloride at 20°C. The polymers are thus obtained in the form of dark-yellow or brown powders partly soluble in chloroform and benzene. The yields are 60 - 70%. Below 450°C, the polyphenylenes obtained are infusible, and contain a crystalline fraction, as shown by X-ray structural analysis. Reaction of dilithium tetraphenyl butadiene-1,3 with arsenic, antimony, and tin halides gives the corresponding heteroderivatives of tetraphenyl cyclopentadiene (Ref. 4: see below). It is shown that the use of titanium tetrachloride, vanadium tetrachloride, vanadium oxychloride, and cobalt chloride yields polydiphenyl acetylene (yield of up to 70%) of limited solubility in chloroform. On reaction with vanadium oxychloride, the soluble fraction is orange-colored, crystalline, and melts at 220 - 240°C. The mean molecular weight as determined with the aid of thermistors is

Card 2/3

28279

S/062/61/000/010/016/018

B106/B101

Use of the reaction of organodilithium...

1560 ± 40. The insoluble fraction of polydiphenyl acetylene is almost colorless, highly crystalline, and melts at 390 - 400°C. All of the above-mentioned polymers give narrow electron paramagnetic resonance signals. Their content of paramagnetic particles per gram is 10^{17} - 10^{18} , which is in agreement with data published on polyphenylene and polydiphenyl acetylene obtained by other methods (Ref. 5: A. A. Berlin, Khimiya i tekhnologiya polimerov, No. 7 - 8, p. 139 (1960)). The present report is a "Letter to the Editor". [Abstracter's note: Complete translation.] There are 5 references. 2 Soviet and 3 non-Soviet. The two references to English-language publications read as follows: Ref. 1: H. Gilman, M. Lichtenwalter, J. Amer. Chem. Soc. 61, 957, 1959; Ref. 4: F. C. Leavitt, a. o., J. Amer. Chem. Soc. 82, 5099 (1960).

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR (Institute of High-molecular Compounds of the Academy of Sciences USSR)

SUBMITTED: July 14, 1961

Card 3/3

S/064/61/000/011/002/007
B101/B147

AUTHORS: Dolgoplosk, B. A., Tinyakova, Ye. I.

TITLE: The present state of the problem of rubber synthesis
(Synthesis of special-purpose rubbers)

PERIODICAL: Khimicheskaya promyshlennost', no. 11, 1961, 52 - 60

TEXT: This is a survey on literature data concerning the synthesis of rubbers resistant to frost, gasoline, heat, heat and gasoline, and of polysiloxane rubbers. There are 4 tables and 78 references: 26 Soviet and 52 non-Soviet. The four most recent references to English-language publications read as follows: R. E. Buddulph, W. R. Longworth, P. H. Plesh, Polymer, 1, 521 (1960); H. Kawai, R. S. Stein, J. Appl. Pol. Sci., 4, 439 (1960); Chem. Eng. News, 38, 107 (1960); C. B. Pierce, Ind. Eng. Chem., 52, 783 (1960).

Card 1/1

LYUBETSKIY, S.G.; DOLGOPLOSK, B.A.; YERUSALIMSKIY, B.L.

Free-radical polymerization of ethylene. Part 1: Kinetics of ethylene polymerisation in a benzene and heptane solution. Vysokom. soed. 3 no.5:734-739 My '61. (MIRA 14:5)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR i Nauchno-issledovatel'skiy institut polimerizatsionnykh plastikov.
(Ethylene) (Polymerization)

25162

S/190/61/003/007/006/021
B101/B208

15 8060

1 AUTHORS: Lyubetskiy, S. G., Dolgoplosk, B. A., Yerusalimskiy, E. L.
TITLE: Ethylene polymerization under the action of free radicals.
in: Acetylene polymerization in the presence of benzene with
the system solvent - monomer being above the critical point
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 7, 1961,
1000-1002

TEXT: It was the purpose of the present paper to study acetylene poly-
merization in the presence of benzene as solvent and azobiscutyric acid
dinitrile as initiator. The system was above the critical point so that
it became comparable to a homogeneous state. Polymerization was carried
out at 70°C. Ethylene contained as impurities 0.5% methane and 0.002% O₂.
at the most. Its partial pressure in the autoclave was kept constant with
an accuracy of 10⁻⁵ atm by periodical supply. The relative viscosity of
the polymer was determined in decaline at 25°C. In the first experimental
series, the pressure was varied between 100 and 150 atm. on the benzene

Card 1/4

25262

3/20/61 10/10/67 10/6/68
200/1000

Ethylene polymerization under the ...

concentration was kept constant at 2.8 mole/l. Intrinsic viscosity (at 100 atm 0.35-0.57, at 500 atm 0.52-0.60) and polymerization rate (100 atm 0.9-1.0 g/l-hr, 500 atm 3.2-3.4 g/l-hr) were found to increase with increasing pressure. More important were the results given in Table 1 at 500 atm, 70°C. but with varied benzene concentration. Complete absence of benzene given, however, lower values of intrinsic viscosity and polymerization rate. 92% of the polyethylene obtained was crystalline and resembled the low-pressure ethylene also in other respects. The authors refer to five papers by western authors. There are 2 tables and 7 references: 1 Soviet-bloc and 6 non-Soviet-bloc. The 5 references to English-language publications read as follows: Z. Laita, J. Polymer Sci., 19, 247, 459, 1959; W. Padgett, E. Perry, J. Polymer Sci., 27, 544, 1959; R. Laird, A. Morell, L. Seed, Disc. Faraday Soc., 22, 126, 1956; R. Heines, W. Bryant, A. Larchar, Industr. and Engng. Chem., 49, 1071, 1957; S. Kodama, V. Matsushima, A. Ueyoshi, T. Shimidzu, J. Polymer Sci., 41, 89, 1959.

Card 2/4

Ethylene polymerization under the ... 25262

S/190/61/003/007/006/021 :
B101/B208

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR
(Institute of High-molecular Compounds AS USSR), Nauchno-
issledovatel'skiy institut polimerizatsionnykh plastikov
(Scientific Research Institute of Polymerization Plastics)

SUBMITTED: September 6; 1960

Card 3/4

DOLGOPLOSK, B.A.; TINYAKOVA, Ye.I.

Present state of knowledge of rubber synthesis (synthesis of rubbers
for special uses). Khim.prom. no.11:79/-802 N '61.

(MIRA 1511)

(Rubber, Synthetic)

30727

S/020/61/141/003/015/021
B101/B117

15.8170

AUTHORS: Piotrovskiy, K. B., Ivanov, A. P., and Dolgoplosk, B. A.,
Corresponding Member AS USSR

TITLE: The role of compounds of metals of varying valency in the
thermal stabilization of polysiloxanes

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 3, 1961, 677-678

TEXT: Assuming that the stabilizing effect of ferric oxide and other
similar compounds was due to a formation of stable complexes with the
active centers of the siloxane chain, the authors studied the effect of
oxides of Fe, Co, and Cu on the anionic polymerization of octamethyl
cyclotetrasiloxane (cyclic tetramer). The anionic polymerization of the
tetramer was conducted at 140°C under the action of 0.0074% by weight of
KOH in N₂ atmosphere. The initial product had a boiling temperature of
64°C/4 mm Hg, $d_4^{20} = 0.9575$. The tetramer was mixed with 10% by weight of

Fe₂O₃, or Co₂O₃, or CuO. At regular intervals, samples were taken,
weighed, dissolved in benzene, the polymer precipitated with methanol, and

Card 1/3

30717

S/020/61/141/003/015/021
B101/B117

The role of compounds of ...

dried in vacuo at 100°C. The following was found: addition of Fe_2O_3 , Co_2O_3 , or CuO completely inhibited the polymerization, also when the oxides were added at a later stage of the process. This is taken as a proof that the presumed formation of stable complexes between metal oxide and active centers did really occur. This constitutes the basis for the stabilizing effect of metal oxides on polysiloxane rubbers at high temperatures. This also inhibits the polymerization process and the destruction process at high temperatures. A report by M. Kušera, M. Jelinek, I. Lanikova, K. Vesely delivered before the International Symposium on Macromolecular Chemistry USSR, M., July 14-18, 1960, Dokl. i avtoref, sekts. 2, 1960, p. 232, is mentioned. There are 2 figures and 6 references: 3 Soviet and 3 non-Soviet. The three references to English-language publications read as follows: British Patent no. 658640 (1950); US Patent no. 2558561 (1951); British Patent no. 643018 (1950).

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

The role of compounds of ...

SUBMITTED: July 26, 1961

30727

S/020/61/141/003/015/021
B101/B117

X

32429

S/020/61/141/006/014/021
B103/B147

15.9201

11.2211

AUTHORS:

Yermakova, I. I., Dolgoplosk, B. A., Corresponding Member
AS USSR, and Kropacheva, Ye. N.

TITLE:

Cis-trans isomerization of the links of 1,4-polybutadiene
under the effect of nitrogen peroxide

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 141, no. 6, 1961,
1363 - 1365

TEXT: The isomerizing effect of NO_2 and its dimer N_2O_4 of hexaphenyl
ethane, and of three disulfides was studied on 2% benzene solutions of
a) cis-1,4-polybutadiene, and b) cis-butene-2 in glass ampullas. The
content of 1,2 or trans-1,4 links in the polymer was calculated on the basis
of the intensity in the maxima 909 and 967 cm^{-1} , respectively, of the
infrared spectra (spectra taken by Z. D. Stepanova). The change of the
cis-trans forms of the butenes was recorded chromatographically during the
process (by A. N. Genkin). It has been found that in case a) the cis-links
of the polymer chain are isomerized to trans-links, i. e., the more inten-
Card 1/3

32429

S/020/61/141/006/014/021
B103/B147

Cis-trans isomerization...

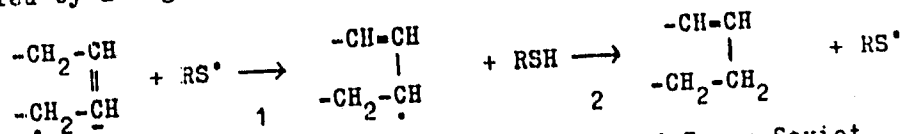
sively the higher the NO_2 concentration. Thus, 23.5 mole% of NO_2 results in a polymer with 60% of trans-links. No isomerization occurred at -50°C owing to the tendency of NO_2 to dimerize below 0°C . Isomerization seems to be effected merely by the NO_2 form. At $+96^\circ\text{C}$ as well as at -50°C , NO_2 is added quantitatively to the double bond. The resulting products are insoluble in a hydrocarbon medium. In case b) similar results were obtained. With a NO_2 concentration of 6 mole%, 40% of cis-butene-2 is converted to trans-butene-2 at 90°C within 2.5 hr. The reaction does not reach the equilibrium state, because NO_2 is consumed by the addition. Neither hexaphenyl ethane at $96 - 130^\circ\text{C}$ nor diphenyl-picryl hydrazyl at 20° and 60°C cause structural changes of the chain in case a). The disulfides decomposing into free radicals at 120°C (Refs. 1 - 4, see below) only lead to gel formation without isomerization, one radical being added to the double bond. It is assumed that the isomerization under the effect of RS^\cdot radicals, which is described in Refs. 1 - 4, does not take place owing to their addition to the double bond, but only when an H atom is broken off from the chain. The mercaptan formed in stage 1 takes part in the chain transfer; this results

32129

S/020/61/141/006/014/021
B103/B147

Cis-trans isomerization...

in the regeneration of the RS^\bullet radicals. Such an isomerization has to be accompanied by a migration of the double bond:



There are 2 figures and 11 references: 4 Soviet and 7 non-Soviet. The four most recent references to English-language publications read as follows: Ref. 1: J. I. Cunneen, F. W. Shipley, J. Polym. Sci., 36, 77 (1959); Ref. 2: J. I. Cunneen et al., Trans. Inst. Rubber Ind., 34, 260 (1959); Ref. 3: J. I. Cunneen, W. F. Watson, J. Polym. Sci., 38, 521 (1959); Ref. 4: J. I. Cunneen, W. F. Watson, ib. 533. ✓

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: August 18, 1961

Card 3/3

S/190/62/004/002/001/001
B110/B:01

AUTHORS: Belonovskaya, G. P., Dolgoplosk, B. A., Chernova, Zh. D.
TITLE: Study of the oxidation of $TiCl_3$ in hydrocarbon and aqueous media
PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 2, 1968, 161 - 166

TEXT: A. N. Nesmeyanov et al. (Dokl. AN SSSR, 95, 813, 1954) has shown that the oxidation of $Ti(OR)_3$ by oxygen proceeds via the free radical $(OR)_3TiO^\cdot$. The oxidation reactions of $TiCl_3$ by oxygen and hydroperoxides were to be studied in connection with the polymerization with Ziegler catalysts. Colloids, 1 - 2 and 8 - 10% solutions of $TiCl_3$ in absolute C_2H_5OH with benzene, acidified with glacial acetic acid were rapidly oxidized by oxygen at 18 - 20°C. In solutions of cis-1,4-polyisoprene (I) and cis-1,4-polybutadiene (II), this caused deep destruction of polymers and a decrease in intrinsic viscosity for I from 2.03 to 1.5, and for II from 3.92 to 2.7. $TiCl_4 \cdot 4C_6H_5NH_2$ was separated during the oxidation of Card 1/4

S/190/62/004/001/00/00
B:10/B:01

Study of the oxidation of $TiCl_3$...

$TiCl_3$ with azobenzene in aqueous and hydrocarbon solutions. The complexes with azobenzene nitro-benzene, aniline, and phenols, which can easily be washed out with water, are water-resistant, and hydrolyze after prolonged storage only. The reaction $TiCl_3 + ROOH \longrightarrow RO^* + HOTiCl_3$

$RO^* + AH \longrightarrow ROH + A^*$, (AH = solvent) takes place with isopropyl benzene hydroperoxide. Thus, 2% benzene solutions of I and II are immediately structuralized at 20°C. Ordinary inhibitors of chain radical processes such as aromatic amines and phenols, as well as nitro-benzene, quinone and other oxidizers inhibit the structuralization. In a homogeneous aqueous solution, polyacrylonitrile is obtained in ~60% yield at 20°C from acrylonitrile in the presence of isopropyl benzene hydroperoxide and $TiCl_3$.

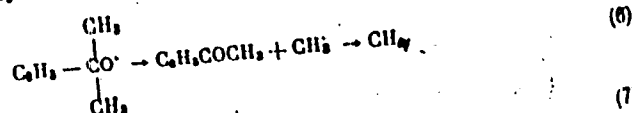
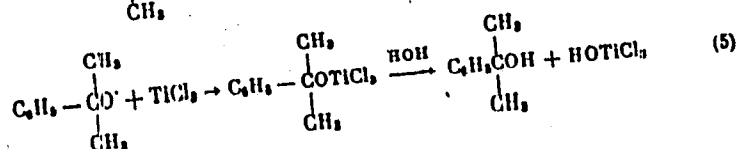
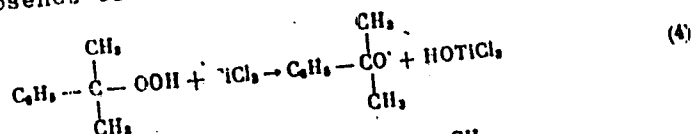
In aqueous solutions, isopropyl benzene hydroperoxide reacts with $TiCl_3$ at a molar ratio of 1 : 2 in the absence of acceptors of free radicals. In the presence of such acceptors, the ratio of the reacting components is ~1. The reaction is stopped at ~70°C. At $\gg 20^\circ C$ and with ~1% hydroperoxide solution, 16-20% CH_4 (referred to hydroperoxide) is separated, which is not the case in the presence of acceptors. 65 - 75% dimethoxy phenyl carbinol

Card 2/4

S/190/62/004/002/001/021
B110/B101

Study of the oxidation of TiCl_3 ...

and 15 - 17% acetophenone are formed at a TiCl_3 : hydroperoxide ratio of 2 : 1 in the absence of acceptors. The reactions:



Card 3/4

S/190/62/004/002/001/021
B110/B101

Study of the² oxidation of $TiCl_3$...

are assumed to take place under the action of $TiCl_3$ with hydroperoxide, (5) and (6) do not occur in the presence of acceptors. There are 2 figures, 5 tables, and 10 references: 6 Soviet and 4 non-Soviet. The reference to the English-language publication reads as follows: M. S. Kharash, A. Fono, W. Nudenberg, J. Organ. Chem., 16, 113, 1951.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds AS USSR)

SUBMITTED: November 24, 1960

Card 4/4

19693

S/190/62/004/004/009/019
B117/B138

5 3830
AUTHORS:

Lyubetakiy, S. G., Dolgoplosk, B. A., Yeruslimskiy, B. L.

TITLE:

Polymerization of ethylene affected by free radicals III.
Polymerization of ethylene with the monomer - polymer system in a non-homogeneous state

PERIODICAL:

Vysokomolekulyarnyye soyedineniya, v. 4, no. 4, 1962,
533-539

TEXT: The polymerization kinetics of ethylene was studied in the presence of azoisobutyric acid dinitrile and benzene between 100-600 atm at 70°C. The activation energy was determined by additional experiments at 60 and 80°C and found to be 17 ± 2 kcal/mole. At relatively low monomer conversion at 100-300 atm, the rate of polymerization has a first-order dependence in relation to monomer concentration. Here the degree of polymerization changes linearly with the monomer concentration. At pressures above 300 atm, the dependence of polymerization rate and molecular weight of the polymer on the monomer concentration shows a marked change after this. The degree of polymerization does not change linearly with the concentration. The dependence of rate and degree of polymerization on the volatility of

S/190/62/004/004/009/019
B117/B138

Polymerization of ethylene...

ethylene is similar. At 400-600 atm, the order of reaction in relation to volatility approaches 1.9. In experiments of up to 20 hr duration, gradual increase of the molecular weight of the polymer and constant polymerization rate were observed. This confirms the concept of "live" polymer chains in polymerization. Their existence was proved by direct experiments at 20°C. The increasing molecular weight clearly showed that the polymerization of ethylene at room temperature develops further on "live" polymer chains. The change of the dependence of degree and rate of polymerization observed at the beginning of the reaction at 300-400 atm is probably connected with the development of an active solid phase. The aggregation of the growing chains, which leads to accumulation of the "live" polymer, plays a decisive role. The change of the polymerization mechanism setting in above 300 atm results in a functional dependence of general form: $k_a = f(\bar{P}_{Pol}) = f([M])$, where k_a is the constant of the rate of aggregation of "live" polymer radicals, \bar{P}_{Pol} is the mean degree of polymerization, and $[M]$ is the monomer concentration. The deviation of the order of reaction in relation to the initiator concentration, which becomes especially noticeable in the absence of the solvent, points to a change of the polymerization mechanism. The

Card 2/3

S/190/62/004/004/009/019
B117/B138

Polymerization of ethylene...

order of reaction of 0.69 was ascertained without solvent, and of 0.53 -0.58 in the presence of benzene (0.14-0.28 mole/l). The increase of polymerization rate and molecular weight of the polymer observed in the presence of small benzene amounts can also be traced back to the growth of "live" polymer chains in the solid phase. There are 6 figures and 4 tables. The two most important English-language references are: R. Buchdal, Disc. Faraday Soc., 22, 150, 1956; C. Bamford, A. Jenkins, M. Symons, W. Townsed, J. Polymer Sci., 34, 181, 1959.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds AS USSR). Nauchno-issledovatel'skiy institut polimerizatsionnykh plastmass (Scientific Research Institute of Polymerization Plastics)

SUBMITTED: March 10, 1961

Card 3/3

X

38280

S/190/62/CO4/OC6/OC6/026
B101/B110

5.3800
AUTHORS:

Tinyakova, Ye. I., Dolgoplosk, B. A., Kuren'gina, T. S.

TITLE:

Polymerization under the action of catalytic systems
containing cobalt or tungsten carbonyls and diethyl
aluminum halide

PERIODICAL:

Vysokomolekulyarnyye soyedineniya, v. 4, no. 6, 1962,
828-834

TEXT: The authors investigated the catalytic effect of the precipitate
formed when $\text{Co}(\text{CO})_4$ or $\text{W}(\text{CO})_6$ dissolved in hydrocarbons are mixed with
 $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. The following were polymerized with the cobalt complex
(ratio carbonyl : R_2AlCl = 1 : 5): isoprene (20°C , 2.5 hr, polymer yield
31%), butadiene (50°C , 1.5 hr, yield 25%; 2.5 hr, yield 40%), styrene
(20°C , 3 hr, 29.8%), α -methyl styrene (80°C , 42 hr, 47.2%), and n -butene
(50°C , 48 hr, 7%). The investigation of the structure of butadiene
polymerized with the cobalt or tungsten complexes gave the following
results irrespectively of the temperature (40 - 50°C) and of the ratio
Card 1/2

S/19C/62/CO4/006/OC6/C26
B101/E110

Polymerization under the ...

carbonyl : R_2AlCl (1 : 2.5 to 1 : 18): 85-87% cis-1,4 bonds, 5-8% trans-1,4 bonds, and 5-7% 1,2 bonds. Isoprene polymerized with the cobalt complex (20-50°C) contained 61-62% cis-1,4 bonds, 22-23% trans-1,4 bonds, and 14-16% 3,4 bonds. An analysis of the precipitate formed from $Co(CO)_4$ and $Al(C_2H_5)_2Cl$ showed: ratio Co : Al between 1 : 1.25 and 1 : 3; ratio Al : Cl ~ 1 : 1; ratio CO : Co ~ 1; ratio C_2H_5 : Al ~ 1 : 1. Since no gases are released during the formation of the precipitate, a reaction of CO with $Al(C_2H_5)_2Cl$ is assumed, similar to that occurring with organolithium and organomagnesium compounds. The absorption of CO by $Al(C_2H_5)_2Cl$ and the formation of sec-amyl alcohol were proved experimentally. The

formula: $CoCo \cdot AlR_2Cl \cdot R_2C \begin{matrix} \swarrow OAl(R)Cl \\ \searrow Al(R)Cl \end{matrix}$ is suggested for the catalytic complex

There are 1 figure and 3 tables.

ASSOCIATION: Institut vysokomolekulyarnykh soedineniy AN SSSR (Institute of High-molecular Compounds AS USSR)

SUBMITTED: April 1, 1961
Card 2/2

S/190/62/004/009/005/014
B101/B144

AUTHORS: Dolgoplosk, B. A., Yeruslimskiy, B. L., Kavunenko, A. P.,
Kerzhur'yeva, A. V.

TITLE: Polymerization of diene hydrocarbons under the action of
organomagnesium compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 9, 1962, 1333-1337

TEXT: The polymerization of butadiene (I), 2,3-dimethyl butadiene (II), and chloroprene (III) by the system $(C_4H_9)_2Mg - C_4H_9MgI$ was studied under the same conditions as that of isoprene described previously (Vysokomolek. soyed., 2, 541, 1960). Results: (1) A solution of 25 - 30 mole% I in hexane yielded ~10% polymer with 77 - 75% 1,4 bonds at 100°C. Under the same conditions, II yielded ~40% polymer with 97% 1,4 bonds. The polymerization proceeds more slowly than that of isoprene. The polymers are completely soluble in benzene and have lost ~6-8% of their double bonds. It is assumed, therefore, that an intramolecular cyclization occurs. (2) The polymerization of III in hexane at 40 - 60°C yielded up to 20% polymer. The polymers had limited solubility in benzene, and their glass transition

S/190/62/004/009/005/014
B101/B144

Polymerization of diene...

point was -46 to -49°C . (3) The consumption of organomagnesium initiators during the polymerization of isoprene was studied. The content in C_4H_{10} liberated by H_2SO_4 was determined chromatographically. The continuous decrease in initiator concentration and the continuous increase in molecular weight during the reaction suggest a consecutive organometal synthesis. Monomer addition to the C-Mg bond is comparatively slow. There are 1 figure and 4 tables.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds AS USSR) ✓

SUBMITTED: May 20, 1961

Card 2/2

S/190/62/004/009/006/014
B101/B144

AUTHORS: Kovalevskaya, R. N., Tinyakova, Ye. I., Dolgoplosk, B. A.

TITLE: A study of heterogeneous catalytic systems on the basis of cobalt oxides or salts and organoaluminum compounds

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 9, 1962, 1338-1344

TEXT: An examination of the polymerization of butadiene or isoprene by catalytic systems consisting, on the one hand, of CoCl_2 , CoBr_2 , CoSO_4 , CoO , on the other hand, of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ or $\text{Al}(\text{C}_2\text{H}_5)_3$ in benzene showed the following results: (1) The reaction takes place at room temperature. Polybutadiene contains up to 90%, and polyisoprene up to 65 - 70% cis-1,4 bonds. (2) Redox reactions do not occur between $(\text{C}_2\text{H}_5)_2\text{AlCl}$ on the one hand and CoCl_2 , CoO , Co_3O_4 on the other hand. The amount of $(\text{C}_2\text{H}_5)_2\text{AlCl}$ in the mixture does not change, and gaseous compounds do not form between 20 and 80°C. The complex which initiates the catalysis has the composition $\text{CoCl}_2 \cdot \text{AlR}_2\text{Hal}$ or $\text{CoO} \cdot \text{AlR}_2\text{Hal}$. (3) The system $(\text{C}_2\text{H}_5)_3\text{Al} + \text{CoO}$ is inactive.

Card 1/2

A study of heterogeneous catalytic...

S/190/62/004/009/006/014
B101/B144

The system $(C_2H_5)_3Al + CoCl_2$ is active only in so far as diethyl aluminum chloride is formed. Without monomers, the reaction followed the equation $2Al(C_2H_5)_3 + CoCl_2 \rightarrow 2Al(C_2H_5)_2Cl + Co + mC_2H_6 + nC_2H_4$, where $m + n = 2$. Since the amount of resulting hydrocarbons is not affected by the solvents gasoline, cumene, and α -methyl styrene, the reaction of $(C_2H_5)_3Al$ with $CoCl_2$ does not pass through radical processes. There are 4 tables.

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High-molecular Compounds AS USSR) ✓

SUBMITTED: May 22, 1961

Card 2/2

41121

S/190/62/004/010/007/010
B144/E186

573820
AUTHORS:

Milovskaya, Ye. B., Dolgoplosk, B. A., Dolgopol'skaya, P.I.

TITLE:

Interaction of organoaluminum compounds with ethyl chloride
in connection with the polymerization process

PERIODICAL:

Vysokomolekulyarnyye soyedineniya, v. 4, no. 10, 1962,
1503-1506

TEXT: A quantitative study of the interaction between triethylaluminum (I) or diethylaluminum chloride (II) with ethyl chloride in octane showed that hardly any reaction takes place below 80°C. On addition of benzene the reaction with I was scarcely affected, but the reaction with II became very intensive; it resulted in the initially colorless solution becoming a yellow, and in demixing. The organoaluminum compound was completely decomposed and HCl separated. Without ethyl chloride no reaction occurred in the presence of aromatic solvents. Maximum

reactions were observed at 20 - 50°C with molar ratios of 3 and 12 between xylene and II, and of 2 between naphthalene and II, the ratio

Card 1/2

ly

S/190/62/004/010/007/010
B144/B195

Interaction of organoaluminum ...

between C_2H_5Cl and II being in both cases 28. The products obtained, $C_2H_5AlCl_2$ and $AlCl_3$, are cationic catalysts. Tertiary amine prevented any reaction of this kind, since it is a stronger complexing agent than the organoaluminum compound. Introduction of 0.5 mole of I per mole of II into the system completely suppressed the reaction, since the $R_3Al + RAlCl_2 \rightleftharpoons R_2AlCl$ equilibrium was shifted toward R_2AlCl , resulting in a reduction of cationic activity. This effect can be used to eliminate cationic processes when polymerization is conducted in the presence of Ziegler catalysts, ethyl chloride, and aromatic hydrocarbons. There are 2 tables.

ASSOCIATION: Institut vysokomolekulyarnykh soedineniy AN SSSR
(Institute of High-molecular Compounds AS USSR)

SUBMITTED: June 12, 1951

Card 2/2

DOLGOPLOSK, B. A.; TINEAKOVA, E. I. [Tinyakova, Ye. I.]

Present state of the problem of rubber synthesis. General purpose
of rubber synthesis. *Analele chimie* 17 no.1:83-108 Ja-Mr '62.

38106

S/020/62/144/002/018/028
B101/B144

15.920/
AUTHORS:

Bresler, L. S., Dolgoplosk, E. A., Corresponding Member AS
USSR, Kolehkovs, M. F., and Kropacheva, Ye. N.

TITLE:

Copolymerization of butadiene with isoprene under the
action of complexes of butyl lithium with triethyl amine or
tetrahydrofuran.

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 144, no. 2, 1962, 347-348

TEXT: C^{14} -tagged butadiene was copolymerized with isoprene using the
anionic complex catalysts $Li-n-C_4H_9 + N(C_2H_5)_3$ (I) and
 $Li-n-C_4H_9 + (CH_2)_4O$ (II). The molar ratio between catalyst and monomer
was 1:300, and that between complexing agent and butyl lithium was 70:1.
Copolymerization was carried out at $20^{\circ}C$ in argon. At a low degree of
conversion, it was interrupted by cooling to $-70^{\circ}C$. The catalyst was
decomposed with ethanol, and the unreacted monomer was distilled off
together with the solvent. The degree of polymerization was determined
from the weight of the polymer dried in vacuo, and the number of butadiene

Card 1/3

S/020/62/144/002/018/028
B101/B144

Copolymerization of butadiene ...

links in the polymer was derived from the C^{14} activity. The copolymerization constants were calculated according to M. Fineman and S. D. Ross (J. Polym. Sci., 5, 259 (1950)). At yields above 10%, the initial monomer concentration was corrected according to C. G. Overberger, D. Tanner, and E. M. Pearce (J. Am. Chem. Soc., 80, 4566 (1958)). Results: With catalyst I, the copolymerization constant was $r_1 = 3.6$ for butadiene, and $r_2 = 0.11$ for isoprene; with catalyst II, $r_1 = 4.5$, and $r_2 = 0.13$. $r_1 = 2.8$ and $r_2 = 0.43$ were obtained by using the Fineman-Ross equation to convert data of G. V. Rakova and A. A. Korotkov (DAN, 119, 982 (1958)) for butyl lithium dissolved in n-hexane. Thus, the relative activity of butadiene during copolymerization with isoprene rises as a function of the solvent: hexane < triethyl amine < tetrahydrofuran.. These findings corroborate the assumption that the $C^{(-)}-Li^{(+)}$ bond is polarized to a greater extent under the action of complexing electron donors. A comparison with data for $R_2Al-TiCl_4$ ($r_1 = 1.0$; $r_2 = 1.0$) and $R_2AlCl-CoCl_2$ ($r_1 = 2.3$; $r_2 = 1.15$) proves the substantial difference in activity between Ziegler and anionic catalysts.

Card 2/3

Copolymerization of butadiene ...

S/020/62/144/002/018/028
B101/B144

There are 1 figure and 1 table.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut
sinteticheskogo kauchuka im. S. V. Lebedeva (All-Union
Scientific Research Institute of Synthetic Rubber imeni
S. V. Lebedev)

SUBMITTED: February 5, 1962

Card 3/3

TINYAKOVA, Ye.I.; ZHURAVIEVA, T.G.; KUREN'GINA, T.N.; KIRIKOVA, N.S.;
DOLGOPLOSK, B.A.

Cation activity of components of complex catalysts. Dokl. AN SSSR.
144 no.3:592-595 14y '62. (MIRA 15:5)

1. Institut vysokomolekulyarnykh soyedineniy AN SSSR. 2. Chlen-
korrespondent AN SSSR (for Dolgoplosk).
(Catalysts) (Polymerisation) (Cations)

S/020/62/144/004/015/024
B101/B138

10.42.1
AUTHORS:

Grechanovskiy, V. A., Dolgoplosk, B. A., Corresponding Member
AS USSR, Kropacheva, Ye. N., Poddubnyy, I. Ya., Sterenzat,
D. Ye., and Khrennikova, Ye. K.

TITLE:

Distribution of molecular weight in stereographically regular
polybutadiene polymerized under the influence of "cobalt"
systems

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 144, no. 4, 1962, 792 - 794

TEXT: Changes in the molecular weight of polybutadiene and in its distribution M_0 were studied in relation to the monomer concentration and degree of polymerization. The polymerization was performed in a 10% solution of the butadiene in benzene, in the presence of a complex catalyst composed of $\text{CoCl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ and $\text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$, the concentration of the CoCl_2 being 0.01 % and that of the dibutyl-aluminum chloride 2% as referred to the monomer. The M_0 was found using an ultra-centrifuge ($\sim 180,000 \text{ g}$), hexane and heptane in equal proportions being thermodynamically almost ideal as

Card 1/3

S/020/62/144/004/015/024
B101/B138

Distribution of molecular weights...

a solvent, and the calculation being done according to S. Ya. Frenkel' (ZhTF, 24, no. 12, 2167 (1954)). Results: (1) With 20% conversion the maximum M_o came at about 245,000. This enabled the number average molecular weight \bar{M}_n to be calculated as 270,000 and the weight average molecular weight \bar{M}_w as 320,000. (2) With 97% conversion M_o was about 90,000, \bar{M}_n was 136,000 and \bar{M}_w was 265,000. Similar results were obtained with the catalyst $CoBr_2 \cdot C_2H_5OH - Al(iso-C_4H_9)_2Cl$. (3) Stepwise addition of the monomer, each successive portion thereof being added only after the preceding portion was completely polymerized, gave $M_o = 55,000$, $\bar{M}_n = 68,000$ and $\bar{M}_w = 180,000$ for all of the successively polymerized portions. Conclusions: (a) The catalyst is fully regenerated and remains active for a long time (>100 hr); (b) the reduced M_o , \bar{M}_n and \bar{M}_w in case (2) is due to reduction in the monomer concentration when polymerization lasts longer; (c) in case (3) two opposite tendencies compensate one another: namely the tendency to higher M_o through the catalyst becoming

Card 2/3

Distribution of molecular weights...

S/020/62/144/004/015/024
B101/B138

diluted by added portions of monomer and the tendency to lower M_o as a result of diminishing butadiene concentration; hence all portions show the same values of M_o , \overline{M}_n and \overline{M}_w . There are 4 figures.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: March 13, 1962

Card 3/3

40387
S/020/62/145/006/011/015
B106/B144

15.9201

AUTHORS: Zgonnik, V. N., Dolgoplosk, B. A., Corresponding Member AS
USSR, Kropachev, V. A., and Nikolayev, N. I.

TITLE: Some regularities observed in the polymerization of butadiene
under the action of catalytic systems containing cobalt

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 145, no. 6, 1962, 1285-1287

TEXT: The authors studied the polymerization of butadiene under the ac-
tion of a homogeneous catalytic system consisting of a cobalt chloride -
pyridine complex and diisobutyl aluminum chloride, using a technique
already described (Vysokomolek. soved., 4, no. 7 (1962)). With benzene
as a solvent, temperatures between 5 and 50°C, and with contents of:
1.2 moles/l butadiene, $2.1 \cdot 10^{-5}$ moles/l CoCl_2Py_2 , $1.5 \cdot 10^{-2}$ moles/l
 $\text{Al}(\text{iso-C}_4\text{H}_9)_2\text{Cl}$, the yield of polymer was $\sim 40\%$. Table 1 gives the
mean values from several determinations of the polymerization rate and
molecular weight of polymer. These correspond with a total activation
energy of 8.2 kcal/mole. The polymerization rate at 20°C is directly
Card 1/3

Some regularities observed in ...

S/O20/62/145/006/011/015
B106/B144

proportional to the monomer concentration between 6 and 23 moles butadiene on the one hand, and to the CoCl_2Py_2 concentration between $9 \cdot 10^{-6}$ and $7.6 \cdot 10^{-5}$ moles/l on the other hand. The molecular weight of the polymer is directly proportional to the monomer concentration. Experiments showed that many molecules of polymer were formed for each molecule of CoCl_2Py_2 . Chain rupture was found to be attended by a regeneration of the active centers. The distribution curves of the molecular weights of polybutadiene samples with a conversion $< 10\%$ showed that the molecular weight increases and the distribution width decreases (M_w/M_n changes from 1.05 to 1.5) when the CoCl_2Py_2 content decreases. When using the catalytic system $\text{CoCl}_2\text{Py}_2\text{-Al(iso-C}_4\text{H}_9)_2\text{Cl}$, the distribution width of the molecular weight was found to increase as polymerization progresses. There are 4 figures and 3 tables. The English-language references are: G. J. Natta, Pol. Sci., 48, 150, 221 (1960); M. Gippin, Rubb. Age, 89, 802 (1961).

Card 2/3

Some regularities observed in ...

S/020/62/145/006/011/015
B106/B144

ASSOCIATION: Institut vysokomolekulyarnykh soyedineniy Akademii nauk SSSR
(Institute of High-molecular Compounds of the Academy of
Sciences USSR)

SUBMITTED: May 7, 1962

Table. 1. Legend: (1) Temperature, °C; (2) moles/cm³·sec.

Table 1.

| 1. $T, ^\circ\text{C}$ | 2. $W \cdot 10^{-3}$ moles/cm ³ ·sec | $M_n \cdot 10^{-3}$ |
|------------------------|--|---------------------|
| 5 | 0,78 | 398 |
| 20 | 2,53 | 159 |
| 35 | 5,02 | 115 |
| 50 | 6,10 | 82 |

Card 3/3

15.9201

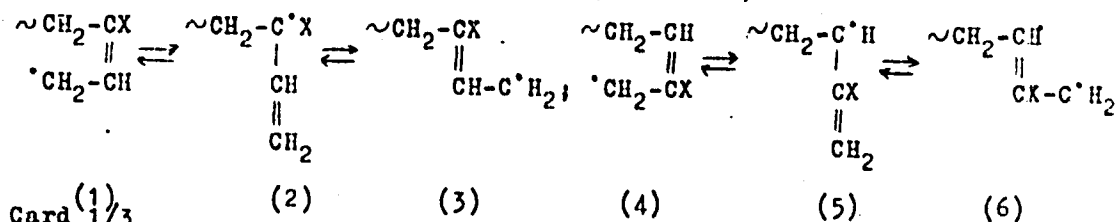
10506
S/020/62/146/002/008/013
B101/B144

AUTHORS: Dolgoplosk, B. A., Corresponding Member AS USSR,
Tinyakova, Ye. I.

TITLE: Polymerization mechanism of dienes and the structure of
the polymer chain

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 146, no. 2, 1962, 362-365

TEXT: The effect produced on the structure of the resulting polymer by
the following configurations of the monomer link at the growing chain end
during the polymerization of butadiene and its 2-derivatives is discussed
on the basis of previous publications (see below):



Polymerization mechanism of ...

S/020/62/146/002/008/013
B101/B144

For radical and cation mechanisms, the configurations (3) or (6) assumed, for polymerization by alkali alkyls, the configurations (2) or (5). Free ions do not form when combined catalysts of the Ziegler type are used.

The formation of 1,4-trans links follows a cationic coordination mechanism (A) $\begin{pmatrix} - \\ + \end{pmatrix} \text{CH}_2 \sim$, and that of 1,2 links follows an anionic coordination

mechanism $[A] \begin{pmatrix} + \\ - \end{pmatrix} \text{CH}_2 \sim$. The former is suited for the polymerization of cationic monomers such as vinyl alkyl ethers and isobutylene, the latter for the polymerization of anionic monomers such as vinyl cyanide, vinyl chloride, etc. In the presence of anionic active centers, it is unlikely that the growing chain end reacts with double bonds in the chain itself to form cyclic side groups. Cis-trans isomerization of the links takes place in radical mechanisms, especially in the cationic mechanism of initiation. In anionic mechanisms it may occur under the action of a cation belonging to the organometallic compound of the catalyst complex. The investigation of these problems in Ziegler-type anionic coordination systems is important. The most important English-language references are: J. Maynard, W. Mochel, J. Polym. Sci., 13, 251 (1954); J. Kuntz, A. Card 2/3

Polymerization mechanism of ...

S/020/62/146/002/008/013
B101/B144

Gerber, J. Polym. Sci., 42, 299 (1960); A. V. Tobolsky, C. E. Rogers,
J. Polym. Sci., 40, 73 (1959); T. S. Lee, I. M. Kolthoff, M. A. Mairs,
J. Polym. Sci., 3, 66 (1948).

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute
of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: June 9, 1962

Card 3/3

S/020/62/146/004/013/015
B117/B186

AUTHORS:

~~Dolgoplosk, B. A.~~, Corresponding Member AS USSR, Tinyakova,
Ye. I.

TITLE:

Mechanism of the action of complex catalysts during polymeriza-
tion

PERIODICAL:

Akademiya nauk SSSR. Doklady, v. 146, no. 4, 1962, 856-859

TEXT: Here the usual assumption that polymerization in the presence of mixed catalysts (such as those of Ziegler, Natta, etc.), is chiefly characterized by a coordination-anion system is challenged. From a number of well-known reactions it can be shown that the cation mechanism too may prevail in polymerization of many systems, which contradicts the concept of chain growth via the C-Al bond. The effectiveness of the cation mechanism is corroborated by: (1) the ability of some mixed catalysts to initiate cis-trans-isomerism in unsaturated polymers and the polymerization of isobutylene, vinyl ether, and β -butene; (2) the positive action of water, HCl, $AlCl_3$, and alkyl halides on the polymerization of some monomers. According to a scheme developed by G. Natta (J. Inorg. and

S/020/62/146/004/013/015
B117/B186

Mechanism of the action of ...

Nucl. Chem., 8, 86, 1960; Tetrahedron, 8, 8 (1960)) fragments of the initial organo-aluminum compound are assumed to remain at one of the ends of the polymer chain, which do not directly participate in the chain growing process but which might be connected with the active centers. This scheme may help to explain the incorporation of organo-aluminum compounds into the polymer chain and the possible development of a cation type polymerization process when an anion type C - Al bond is present. This is an indication of possible participation of organo-aluminum compounds in the chain rupture. It is shown that, when the chain breaks as a result of interaction between the active "cation" end and the inactive "anion" end, annular polymer molecules may sometimes form. In this case, the active center regenerates. The possibility of such a reaction is revealed by the polymerization of butadiene with $\text{TiCl}_4 - \text{R}_2\text{AlCl}$, whereby a cyclic trimer is obtained in an almost quantitative yield. This may be taken as proof that the two carbon ends of the chain are oppositely charged. It is noted that the statement made above does not exclude the anion type of some coordination systems, for example, organo-aluminum compounds and alkoxy compounds of titanium and molybdenum. The polymerization of these compounds presumably takes place via the

Card 2/3

Mechanism of the action of ...

S/020/62/146/004/013/015
B117/B186

δ-δ+
C-Me bond.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute
of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: June 9, 1961

Card 3/3

TURNOV, B.S.; VINOGRADOV, P.A.; DOLGOPLOSK, B.A.; KHRANINA, Ye.N.; KOSTINA, S.I.

Effect of ethers on the chain structure in the stereospecific polymerization of butadiene. Dokl. AN SSSR 146 no.5:1141-1142 0 '62.

(MIRA 15:10)

1. Yaroslavskiy zavod sinteticheskogo kauchuka. 2. Chlen-korrespondent AN SSSR (for Dolgoplosk).

(Ethers)

(Butadiene)

(Polymerisation)

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPILOSK, B.A., red.; YENIKOLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTKOV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, D.A., tekhn. red.

[Heterochain high-molecular weight compounds] Geterotsepnys vysokomolekuliarnye soedineniya; sbornik statei. Moskva, Izd-vo "Nauka," 1963. 246 p. (MIRA 17:3)

KOLESNIKOV, G.S., otv. red.; ANDRIANOV, K.A., red.; DOGADKIN, B.A., red.; DOLGOPLOSK, B.A., red.; YENIKLOPYAN, N.S., red.; KARGIN, V.A., red.; KOZLOV, P.V., red.; KOROTKOV, A.A., red.; KORSHAK, V.V., red.; LAZURKIN, Yu.S., red.; MEDVEDEV, S.S., red.; MIKHAYLOV, N.V., red.; PASYNSKIY, A.G., red.; SLONIMSKIY, G.L., red.; SMIRNOV, V.S., red.; TSVETKOV, V.N., red.; FREYMAN-KRUPENSKIY, K.A., tekhn. red.

[Carbochain high-molecular weight compounds] Karbotsepyne vysokomolekuliarnye soedineniia; sbornik statei. Moskva, Izd-vo AN SSSR, 1963. 287 p. (MIRA 17:1)

B/190/63/005/003/011/024
B101/B186

AUTHORS: Bresler, L. S., Dolgopletskiy, A., Koleshkova, M. P.,
Kropacheva, Ye. N.

TITLE: Copolymerization of butadiene with isoprene under the effect
of the complex organometallic catalysts

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 3, 1963, 357-362

TEXT: A study was made of the copolymerization of butadiene with isoprene under the effect of the heterogeneous system (I) from triisobutylaluminum and titanium tetrachloride and of the homogeneous system (II) from diisobutylaluminum chloride and the cobalt dichloride - ethanol complex in argon atmosphere. Butadiene was tagged with C^{14} so that the composition of the copolymer could be determined from its radioactivity. With system I copolymers were obtained the composition of which with regard to the content of 1,2-, 3,4-, and 1,4-isoprene, trans-1,4 and cis-1,4-butadiene links did not differ from the homopolymers. With system II copolymers with increased content of 1,2 links were formed. The copolymerization was proved by comparison with a mechanical mixture of the two components. For the copolymers a linear dependence of the glass transition point on the

Card 1/2

Copolymerization of butadiene with...

S/190/63/005/003/011/024
B101/B186

composition was observed. T_g increased from -110°C for 100% butadiene to -71°C for 100% isoprene. Also the elasticity curves showed only one minimum for the copolymers, whereas the mixtures had two minima corresponding to the content of the respective two components. For system I the relative activity of butadiene (r_1) as well as of isoprene (r_2) is 1.0 ± 0.05 . For system II $r_1 = 2.3 \pm 0.1$ and $r_2 = 1.15 \pm 0.05$. There are 4 figures and 3 tables.

ASSOCIATION: Nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S. V. Lebedeva (Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev)

SUBMITTED: August 13, 1961

Card 2/2

KROPACHEV, V.A.; ALFEROVA, L.V.; DOLGOPLOSK, B.A.

Polymerization of 3,3'-bis-(chloromethyl) oxacyclobutane in
polar solvents. Vysokomolekul. soed. 5 no.7:994-996 J1 '63.

(MIRA 16:9)

1. Institut vysokomolekulyarnykh soedineniy AN SSSR.
(Oxetane) (Polymerization)

L 18822-63

EPR/WWP(j)/EPF(c)/EWI(m)/BDS. AFFTC/ASD Ps-4/Fc-4/Pr-4

RM/WW/MAY

ACCESSION NR: AF3001043

S/0026/63/000/005/0030/0035

AUTHOR: Dolgorosk, B. A., Corresponding Member of the Academy of Sciences of the SSSR, (Moscow)

TITLE: New ways of synthesizing rubber

SOURCE: Priroda, no. 5, 1963, 30-35

TOPIC TAGS: Cis-polybutadiene, cis-polyisoprene, stereospecific polymerization, water-emulsion medium, Polyurethane, fluorine rubber, silicon-organic substance

ABSTRACT: ¹⁵ Cis-polybutadiene ("SKD rubber") and cis-polyisoprene ("SKI rubber", analogous to natural rubber in structure and properties) have been synthesized on the basis of catalytic systems of stereospecific action. SKD, while inferior to natural rubber in strength and technological properties, considerably surpasses it in resistance to wear and is equal to it in elastic properties, hence for use in tires. Both will early become the main kinds of highly elastic rubber for general use. The stereospecific-polymerization processes in hydrocarbon solutions, particularly SKI and SKD, are technologically complicated by high viscosity of the medium and the great heat effect of polymerization. Development of simplifying systems of polymerizing in water-emulsion media is most urgent. Polyurethane rubbers have

Card 1/3

L 18822-63

ACCESSION NR: AP3001043

S/0026/63/000/005/0030/0035 4

extremely high wear resistance, but have not yet been properly developed due to great technological difficulties and high cost. To convert polyethylene into highly elastic rubber its structure has to be "ruined", e.g. by introducing during polymerization a certain amount of "foreign" links preventing crystallization, e.g. 25-30% propylene. Such rubber is very resistant to oxidizing aging at high temperatures. The valuable complex of properties, together with the availability and cheapness of the raw material, make this type very promising for various purposes. Thus far there is no way to synthesise rubberlike polymers satisfying all conditions imposed by the machine industry, jet engines, intensive radiation, etc. Fluorine rubbers¹⁵ with a carbon polymer chain, combining high heat resistance with chemical inertness, have become important. The hydrogen atoms in ethylene can be entirely or partly replaced by fluorine atoms. Polymerization of these monomers produces crystalline substances with a high melting point; but they are essentially rubbers, since their temperature of vitrification is below 0°. The as yet unsolved problem of synthesizing rubbers capable of standing temperatures above 300°C for a long time can be solved not only by new organo-elemental and inorganic polymers, but also by stabilizers preventing oxidation and chain decay of polymers at high temperatures, e.g. high-temperature oxides of iron, lead and certain other metals acting on products from silicon-organic substances. Orig. has 11 structural diagrams and

Card 2/3

L 18822-63

ACCESSION NR: AP3001043

1 table.

ASSOCIATION: Academy of Sciences of the USSR

SUBMITTED: 00

DATE ACQ: 24Jun63

ENCL: 00

SUB CODE: CH, MA

NO REF SOV: 000

OTHER: 000

Card 3/3

BYSTRICKY, Karel; FARKA, Vladimir

Coal of required quality, a condition of its effective use.
Uhli 5 no.2:61-63 F '63.

1. Odbytové sdružení paliv (for Bystrický). 2. SPK Praha (for Farka).